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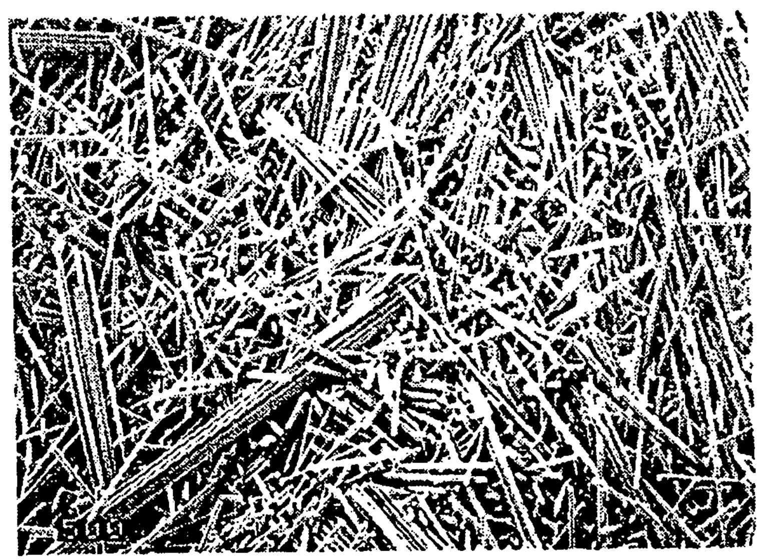
(54) Title: RECOVERY OF CARBON FIBERS FROM EPOXY WASTE

(57) Abstract

Burning off the epoxy resin from graphite-epoxy composite waste to recover carbon fibers provides a method to recover the fibers substantially intact and without the use of chemical solvents. The waste is heated to a temperature in the range of about 375 °C to about 600 °C for a time sufficient to decompose the epoxy through oxidation.



100X 100μm

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RECOVERY OF CARBON FIBERS FROM EPOXY WASTE

This invention relates generally to methods for recovering carbon fibers. More particularly, the invention relates to methods for recovering carbon fibers from graphite-epoxy machining waste.

Graphite-epoxy composite materials containing carbon fibers are used in military ordnance because of their high strength-to-weight and high modules to weight ratios. For example, such composites are used in discarding sabots for kinetic energy projectiles such as 120mm KE anti-tank rounds. The large volume of such ordnance produced results in a significant quantity of machining scrap. Some estimates are that there is about a billion dollars worth of carbon fibers in such machining scrap.

Until the present invention, there has been no known method for recovering the carbon fibers from such waste. The problem has been to separate the fibers from the epoxy resins in which they are contained.

Attempts to date have apparently been unsuccessful because the fibricity of the fibers has been destroyed in the recovery process. Apparently attempts to date have centered around chemical solvents and have involved trying to selectively dissolve the epoxy without damaging the carbon fibers, but such attempts have been unsuccessful.

A new technical approach is needed which can separate the carbon fibers from the surrounding epoxy without significantly weakening the carbon fibers.

These problems are solved in the process of the present invention described and claimed below in which the graphite-epoxy composite material is heated to a critical temperature range and held

there a certain time, so as to decompose and oxidize the epoxy resin without degrading the carbon fibers.

The invention stems from the understanding that the carbon fibers burn at a higher temperature than the epoxy resin and that the carbon fibers are not significantly degraded at the burning temperature of the epoxy resin. The invention thus solves a significant environmental problem in an extremely simple and effective way to give the potential for recovering over a billion dollars worth of valuable and expensive carbon fibers.

Composites containing the carbon fibers have been in use for several decades without this unexpectedly effective simple solution having been discovered, so this solution has not been obvious to those of ordinary skill in the art. It simply has not previously been thought that one could save the carbon fibers by burning them.

The invention will be better understood by referring to the accompanying drawings, in which:

Figure 1 is a scanning electron microscope (SEM) photograph of the graphite-epoxy resin composite after thermal treatment by the method of the invention.

Figure 2 is a SEM photograph of the resin of Figure 1 before thermal treatment.

Figure 3 is a line graph showing the experimentally calculated percentage weight loss of graphite-epoxy resin held at various temperatures for one hour.

Figure 4 is a line graph showing the percentage weight loss of graphite-epoxy resin when held for varying times at 400°C.

Carbon fiber/epoxy composite materials are being extensively used in structures where light weight, high strength, and high stiffness ar

desired or required. In most applications, the composite material is fabricated to a "near-net" condition and various degrees of machining take place after the curing operation to complete the article. In large volumes, the composite machining waste constitutes a considerable value in unclaimed carbon fiber. Samples of machining waste were analyzed, and indeed found to contain a high volume fraction (>60%) of the expensive carbon fibers. Hence it is worthwhile to recover these carbon fibers, and investigate potential "recycle" markets.

It has been found that if the composite waste is heated in air at temperatures in the range of 375° - 600°C for varying periods of time, that enough energy can be obtained to effect epoxy resin decomposition (oxidation) without degrading the carbon fibers. (See Figures 1 and 2). This thermal treatment breaks down the epoxy resin into the volatile compounds, which evaporate and leave clean carbon fibers behind. It is believed that aeration during the treatment will enhance the loss of epoxy, while also promoting the formation of environmentally sound compounds, i.e. CO_2 and H_2O. Thermally treated waste was observed by Scanning Electron Microscopy (SEM) analysis, and showed that the carbon fibers had a surface quality equivalent to the untreated carbon fiber. (See Figure 2).

The temperature used for treating the waste is critical. If the heat treatment is carried out at lower temperatures, significant portions of the epoxy remain attached to the fibers, even when held for extended time periods. This was experimentally observed at the 300°C temperature level. Above 600°C, the fiber oxidation reaction begins to accelerate, as monitored by excessive fiber weight loss.

Time at temperature is also important for complete removal of the epoxy. At an optimum temperature of 400°C, a 30 minute soak is insufficient to remove all resin, whereas a two hour period appears to eliminate most of the epoxy (Figure 2). These factors will also depend upon other variables such as volume of waste material being treated, pan type and size, atmosphere being used, and air flow rates.

The preferred temperature range for burning off the epoxy resin used in the composites for 120mm KE ammunition sabots is 400-500°C. The objective is to burn off the epoxy with minimum damage to the carbon fibers. Likewise the time at which the materials are held at the burning temperature should be enough to be sure essentially all the epoxy is burnt off and no longer, as any longer merely wastes energy. The preferred time is about 4 hours for the machining scrap from 120mm KE ammunition sabots.

The preferred process would use an afterburner to oxidize any volatilized epoxy resin compounds, so that only fully oxidized compounds are released to the atmosphere.

EXAMPLES

Example 1:

Five samples of graphite-epoxy resin composite waste from machining of 120mm KE ammunition sabots (plastic sheaths used in anti-tank ammunition) were heated to and held for one hour at, respectively, 300°C, 400°C, 500°C, 600°C, and 700°C. The composite samples were known to contain about 69% (by weight) carbon fibers and about 31% by weight epoxy resin. The weight loss resulting from this heating is shown in Figure 3. The data indicates that all the epoxy resin is burnt off in one hour at about 450°C.

Example 2:

Four samples identical to those in Example 1 were heated to 400°C and held there for times, respectively, of ½, 1, 2, and 4 hours. The results are shown in Figure 4. It is seen that after about 4 hours, no further significant change in weight in, noted and the weight loss is equal to the calculated weight % of epoxy resin (31%). This indicates that at 4 hours, substantially all the resin is gone and substantially all the carbon fibers remain.

While the invention has been described above and below with references to preferred embodiments and specific examples, it is apparent that many changes, modifications and variations in the materials, arrangements of parts and steps can be made without departing from the inventive concept disclosed herein. For example, in employing the heating method of the present invention to fiber-epoxy resin systems with different particle sizes and different specific resins, the preferred temperature may vary. Simple weight loss experiments can be run to analyze the amount of material decomposed and volatilized during the burning process. The weight loss data from such experiments can be compared with the known percentage by weight of carbon fibers in the composite to determine the amount of epoxy left, if any. The burning time and temperature can then be adjusted to an optimum amount to obtain nearly complete burning of the epoxy. Scanning electron microscope analysis of the residual material can be employed to confirm that carbon fibers are still intact after the burning process. Similarly, the medium in which the burning occurs can be varied to determine if a particular medium produces better r covery. Since the really significant discovery in

the present invention is that the fibers can be recovered from the composite by burning the composite at a temperature within a certain range.

Accordingly, the spirit and broad scope of the appended claims is intended to embrace all such changes, modifications and variations that may occur to one of skill in the art upon a reading of the disclosure.

IN THE CLAIMS:

1. A method of recovering carbon fibers from graphite-epoxy composite materials, characterized by the steps of:

a.) heating the composite materials to a temperature within the range of from about 375° to about 600° Centigrade, and

b.) maintaining the materials within the range for a time period sufficient to remove the desired percentage of epoxy resin.

2. The method of claim 1, characterized in that the materials are maintained within the range for at least two hours.

3. The method of claim 2, characterized in that the materials are maintained within the range for at least four hours.

4. The method of claim 2, characterized in that the materials are maintained within the range for no more than about eight hours.

5. The method of claim 1, characterized in that the materials are heated to a temperature within the range of from about 375°C to about 500°C.

6. The method of claim 1, characterized in that the materials are heated to a temperature within the range of from about 400°C to about 500°C.

7. The method of claim 1, characterized in that the materials are in an air environment during the heating and maintaining steps.

8. The method of claim 1, characterized in that the step of heating the vapors resulting from the material heating and maintaining steps in an oxygen-containing gas to a temperature sufficient to fully oxidize the vapors is included.

100X 100µm

FIG. 1

100X 100µm

FIG. 2

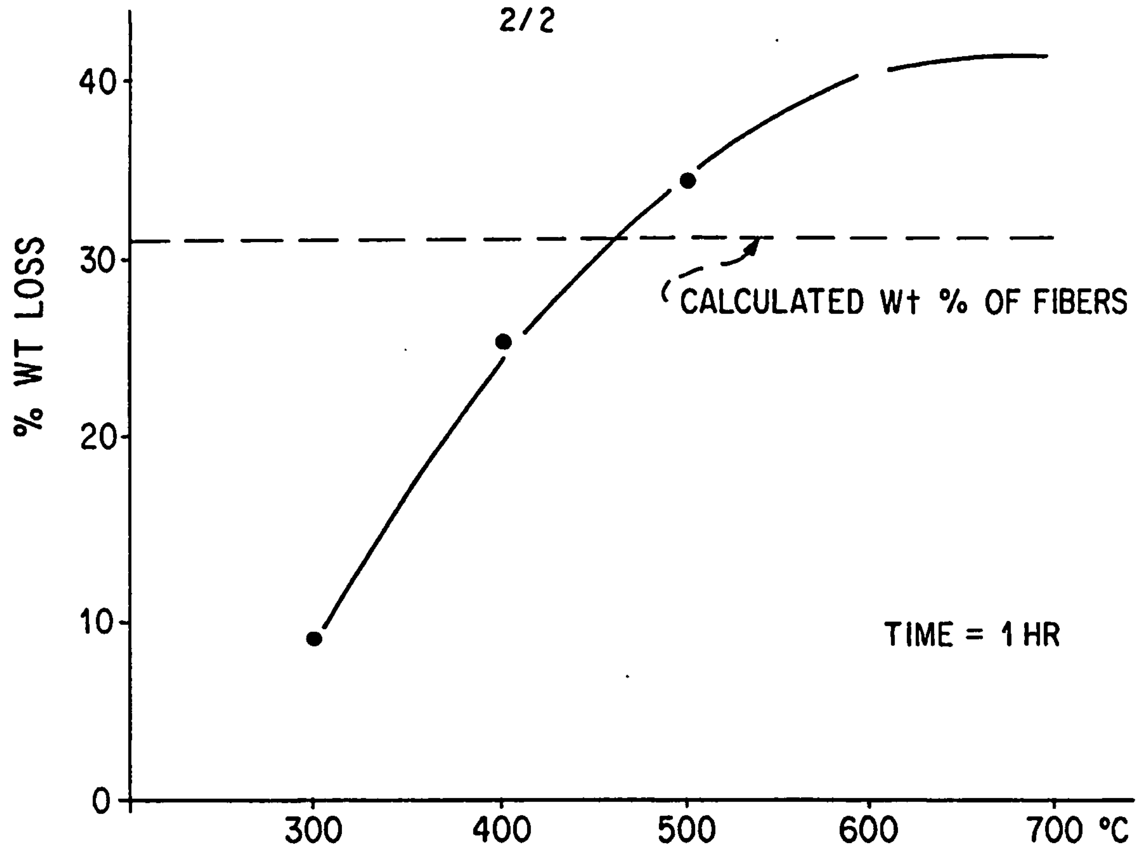
% WT LOSS
40
30
20
10
0
300
400
500
600
700 °C
CALCULATED Wt % OF FIBERS
TIME = 1 HR

FIG. 3

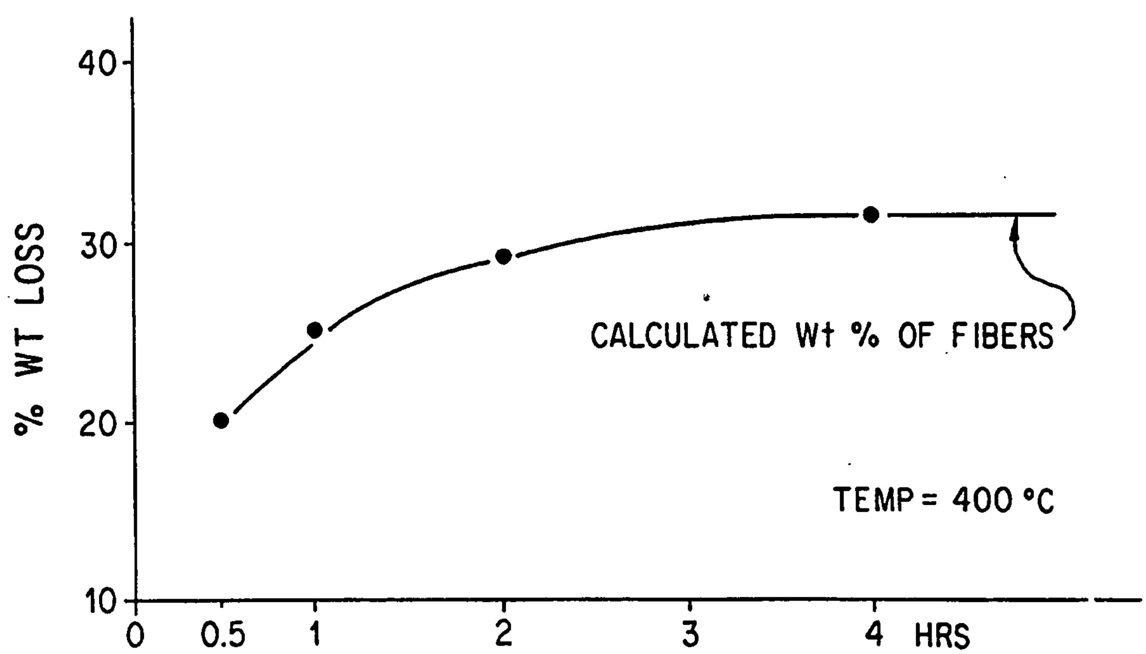
% WT LOSS
40
30
20
10
0
0.5
1
2
3
4 HRS
CALCULATED Wt % OF FIBERS
TEMP = 400 °C

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/11715

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :D01F 9/12; C01B 31/02
US CL :423/447.1, 447.2, 461
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/447.1, 447.2, 461, 460, 445

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS (waste, scrap, epoxy, recover, recycle, salvage, graphite)
CAS ONLINE (waste, scrap, tire, rubber, epoxy, fiber recover, recycle, salvage)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	Lederer et al., "Recycling of Fibre-Reinfoced Duroplastics," Radex-Rundschau, Vol. 3/4, November 1991, see pages 537-540.	1, 5, 6 ---------- 2-4, 7-8
Y	Freeman, Standard Handbook of Hazardous Waste Treatment & Disposal, pages 8.91 -8.97, especially page 8.92, 8.96, Table 8.7.1, 1989.	7-8

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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